# Interactions Among Ligand Production, Chemical Complexation and Speciation, Algal Accumulation, And Sediment-Water Cycling Of Toxic Metals In A Major US Naval Harbor (Elizabeth River, VA)

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## LONG-TERM GOAL

Our long-term goal is to determine the processes controlling the concentrations, chemical complexation and speciation, biological uptake, and cycling of pollutant metals in the water column and sediments of anthropogenically-impacted harbors.

## OBJECTIVES

In conjunction with other ONR HP investigators, we are performing an integrated study of the biogeochemical cycling of Cu, Cd, Zn, and Mn in the water column and sediments of a major US Naval harbor, the Elizabeth River (VA). We are studying the interrelationships among:
(1) trace metal concentrations, complexation and speciation (Donat); (2) *in situ* production of Cu chelators by natural microbial populations (in collaboration with A. Gordon/J. Donat [ODU]); (3) phytoplankton metal uptake (in collaboration with W. Sunda/S. Huntsman [NOAA]); and (4) fluxes of metals and chelators from sediments (Donat and Burdige).

## APPROACH

Our approach consists of both field and laboratory efforts. In conjunction with other Harbor Processes PIs (Gordon, Sunda, Buessler), we performed two major field studies of the Hampton Roads/Elizabeth River in July '99 and in May ‘00. Water column total and dissolved metal concentrations were determined by graphite furnace atomic absorption after APDC/DDDC chelation/chloroform extraction (Bruland et al., 1979; Statham, 1985). In our benthic flux samples, total dissolved Cu concentrations were determined by chemiluminescence (Sunda and Huntsman, 1991), and total dissolved Zn and Cd concentrations were determined by differential pulse anodic stripping volatmmetry (DPASV) at a hanging mercury drop electrode (HMDE) after UV photooxidation (Donat and Henry, 1997). Cu complexation was determined in the water column by competing ligand (salicylaldoxime)

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14. ABSTRACT
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equilibration/adsorptive cathodic stripping voltammetry (Campos and van den Berg, 1994; Bruland et al., 2000), and in the benthic flux samples by DPASV at an HMDE (Donat et al., 1994). Zn and Cd complexation in the water column was determined by DPASV at a thin mercury film rotating glassy carbon disk electrode (Bruland, 1989, 1992), and in the benthic flux samples by DPASV at an HMDE (Donat et al., 1994). Benthic fluxes were determined using core incubation techniques (Burdige and Homstead, 1994; Skrabal et al., 1997; Burdige and Zheng, 1998).

## WORK COMPLETED

We performed our second major field study of the Elizabeth River in May '00, in conjunction with the Gordon/Donat and Sunda/Huntsman projects. Our group of PIs (Donat, Burdige, Gordon, Sunda, and Huntsman) were joined by researchers from Ken Buesseler's lab (WHOI) who are studying groundwater inputs to the Chesapeake Bay/Elizabeth River, and from Beth Ahner's group (Cornell) who are studying the distributions of phytochelatins (algal-produced metal complexing ligands). We provided laboratory space, analytical instrumentation, and equipment (courtesy of ODU's Dept. of Chemistry), and ship time to the Sunda, Buesseler, and Ahner groups during this two-week-long field study.

In May '00, we collected surface water samples along a 7-station estuarine transect from Hampton Roads up the Elizabeth River, and from 1 station in the James River, and collected bottom water and sediment core samples from 2 of these stations in the Elizabeth River. We completed the following determinations for water column and benthic flux samples from both July '99 and May '00 cruises: total (unfiltered) metal (Cu, Cd, Zn, Mn); total dissolved (filtered) metal (Cu, Cd, Zn, Mn); complexation and speciation (Cu, Cd, Zn).

Between 2000 and 2001, we gave 23 presentations on our Harbor Processes Research, of which 8 were published abstracts. These included invited presentations on this ONR HP-funded Elizabeth River work at the San Diego Bay Marine Sediment Processes Workshop (June 2000, San Diego), at the Second Workshop on the Chemistry, Toxicity, and Bioavailability of Copper and Its Relationship to Regulation in the Marine Environment (Nov. 2000), at the Symposium on Pollution Prevention from Ships and Shipyards at the Oceanology International 2001 Conference (May 2001), at EPA's 24$^{th}$ Annual Conference on Analysis of Pollutants in the Environment (May 2001), at ONR's Harbor Processes Review (June 2001), and at the Workshop on the Biotic Ligand Model as a Regulatory Tool for Metal Loadings to Coastal Marine Waters (July 2001). We will also be presenting our results at the International Conference on Remediation of Contaminated Sediments (Venice, Italy; Oct. 2001) and at the Nov. 2001 SETAC Conference (Baltimore).

## RESULTS

**Water Column -** Dissolved (0.22µm-filtered) concentrations of Cu, Cd, and Zn generally increased along the transect from Hampton Roads Harbor (Stn 3) up the Elizabeth River. Dissolved Cu (Fig. 1) ranged from 6nM (Stn 3) to 50nM (Stn 8). Dissolved Cd (Fig. 1) ranged from 94pM (Stn 3) to 560pM (Stn 6), then decreased further upstream to 475pM (Stn 9). Dissolved Zn (Fig. 1) ranged from ~5nM (Stn 3) to 165nM (Stn 8), then decreased upriver to 75nM at Stn 9.

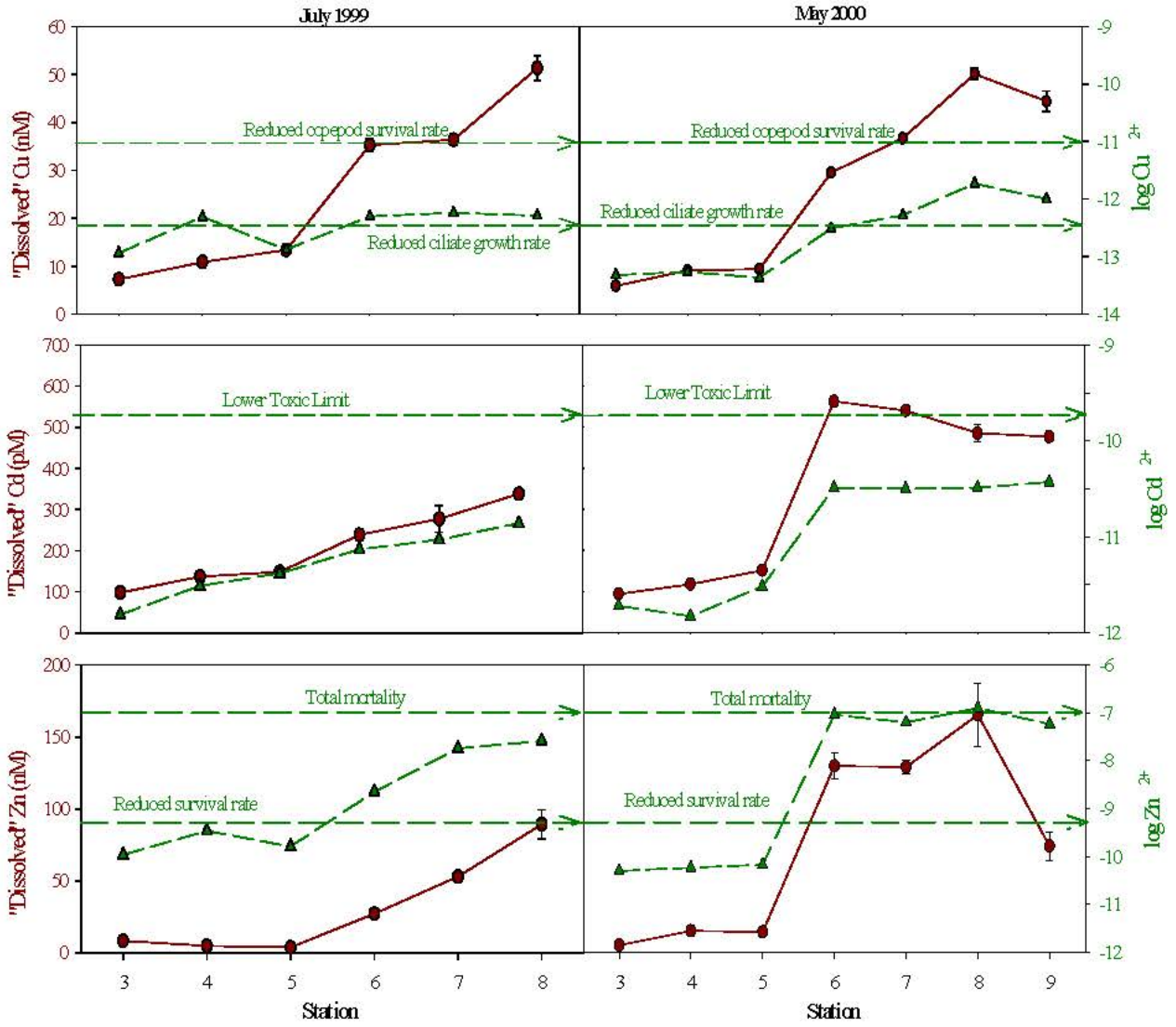


***Figure 1. Concentrations of dissolved (—●—) and free metal ions (—▲—) in the Elizabeth River, July 1999 and May 2000.***

In all surface water samples, dissolved Cu was observed to be >99.9% complexed by one strong organic ligand class (log $K_{Cu2+}$' ~12.2) whose concentration exceeded that of dissolved Cu by 2-10 fold at all stations. The resulting free $Cu^{2+}$ ion concentrations (the potentially toxic form) ranged from 0.042-1.9 pM (Fig. 1). All free $Cu^{2+}$ ion concentrations are below the lower limit concentration of 4 pM reported to reduce the growth rate of a Cu-sensitive ciliate, and are well below the free $Cu^{2+}$ ion concentration of 40 pM reported to reduce the survival rate of a common estuarine copepod (Sunda et al., 1990).

The extent of organic complexation of dissolved Cd in surface water samples ranged from ~0 %(Stn 9) to ~80%(Stn 4). At Stns 3, 4, and 5, two Cd ligands were detected. The concentration of the stronger (log $K'_{Cd'}$ ~ 10) ligand, $L_1$, ranged from 230 nM (Stn 5) to 380nM (Stn 3), and the concentration of the weaker (log $K'_{Cd'}$ ~ 9 ) ligand, $L_2$, ranged from 530 nM (Stn 3) to 780 nM (Stn 4). Only $L_2$ was

detected at Stns 6-8. $L_2$ concentrations were highest (1580 nM) at Stn 6, then decreased further upriver to 320 nM at Stn 8. The concentrations of $L_1$ and $L_2$ exceeded that of dissolved Cd at all stations where each was detected, except Stns 8 and 9. Free $Cd^{2+}$ ion concentrations increased upriver from 1.5 pM at Stn 4 to 37pM at Stn 9 (pCd range: 11.8 to 10.4). The highest free $Cd^{2+}$ ion concentrations are below the concentration of ~ 150pM reported by Brand et al. (1986) to reduce the reproductive rate of the most Cd-sensitive neritic phytoplankton species they tested.

**Benthic Fluxes** - We performed benthic flux studies at two sites in the Elizabeth River - sta. 5 (near Norfolk Naval Base) and sta. 8 (southern branch of the Elizabeth River near Norfolk Naval Shipyard). We recently completed sample analyses from the May '00 study and will shortly complete data processing. We present our results from the July '99 study, and compare these with similar flux studies we did at a site near sta. 5 (sta. PP; Byers, 1999) and at two sites in the mainstem of Chesapeake Bay (Skrabal et al., 1997).

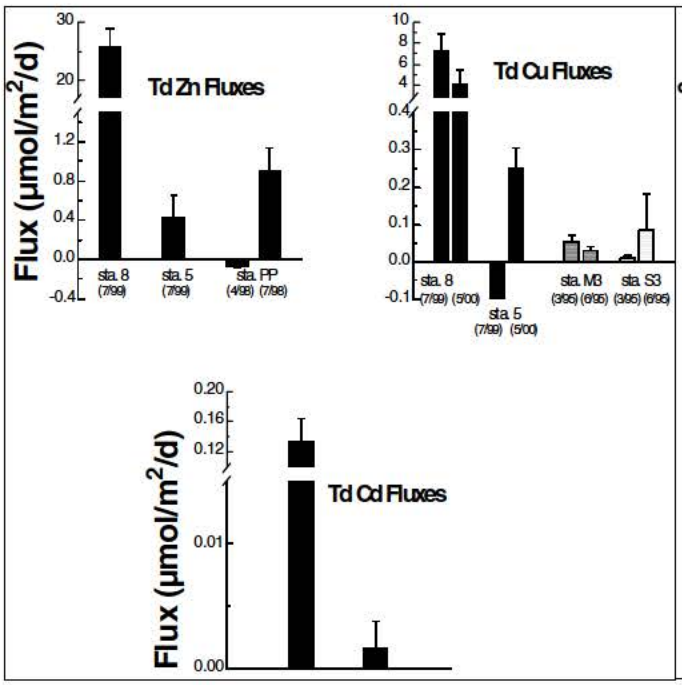


***Figure 2. Total dissolved metal fluxes from stations 5, 8 and PP in the Elizabeth River and stations M3 and S3 in the Chesapeake Bay.***

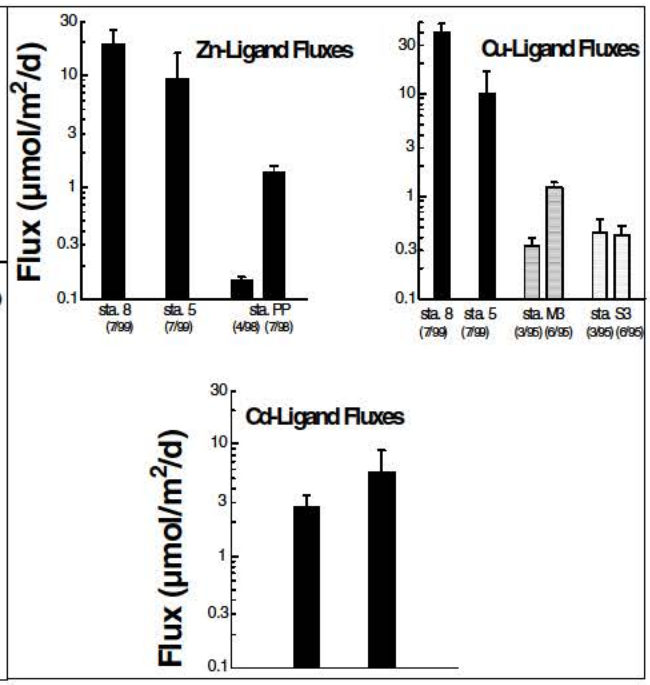


***Figure 3. Fluxes of metal-complexing ligands from station 5, 8 and PP in the Elizabeth River and stations M3 and S3 in the Chesapeake Bay.***

In the Elizabeth River, we observed that: TDZn fluxes > TD Cu fluxes >TD Cd fluxes (Fig. 2), consistent with metal concentrations in these sediments. Furthermore, at all sites for almost all metals, ligand fluxes exceed metal fluxes (compare Figs. 2, 3). Metal and ligand fluxes are generally greater at sta. 8 than at sta. 5. Similar trends are seen in benthic DOC and $\sum CO_2$ fluxes, and suggest a linkage between metal and metal ligand fluxes and sediment carbon remineralization processes. Finally, ligand fluxes appear to be uncoupled from metal fluxes.

With these data we have begun to examine the controls on metal and metal-complexing ligand benthic fluxes. We start with the assumption that these fluxes are likely controlled by metal chemistry (aqueous chemistry and solid phase speciation), sediment metal loadings an/or sediment organic matter remineralization processes. As mentioned above, a positive relationship appears to exist between metal and ligand fluxes, and sediment carbon remineralization processes--we are exploring this relationship in more detailed analyses of the data. We have also begun to examine the relationship between these fluxes and sediment metal loadings. A positive relationship appears to exist between TDCu and Cu ligand fluxes and sediment Cu enrichment factors. For the other metals however, the results are equivocal, partly because of the small sample set. In the next few months we will continue such comparative analyses of metal and metal-complexing ligand fluxes (incorporating the May 2000 flux data into the analysis) to better understand the controls on these fluxes.

## IMPACTS

The information we are producing on the water column complexation and speciation of the toxic metals Cu, Cd, and Zn, and of the micronutrient metal Mn, and on the benthic fluxes of these metals and their ligands are the first such data for the Elizabeth River/Hampton Roads Harbor (home of the US Atlantic Fleet), an area which has been heavily contaminated by pollutant metals from a variety of civilian and military sources.

Metal accumulation by phytoplankton is important both for metal entry into the food chain and metal transport to the sediments. However, the uptake and effects of toxic metals are controlled by their free ion concentrations. Our metal complexation and speciation data will enable us to predict algal uptake, physiological effects, and biogeochemical cycling of these metals. Our data show that while dissolved Cu and Cd concentrations increased upriver by 10x and 6x respectively, the potentially-toxic free $Cu^{2+}$ and free $Cd^{2+}$ concentrations increased upriver by 40x and 25x respectively. However, despite the greater increase in the free ion relative to the total dissolved concentrations of these metals, even the highest free $Cu^{2+}$ and free $Cd^{2+}$ ion concentrations we measured were below reported toxic levels.

The speciation of metals in sediment porewaters governs both their fate (by controlling the extent and speed of their cycling between sediments and the water column), and their effects on biota (by influencing bioaccumulation and toxicity). Sediment-water exchange of both metals and their complexing ligands can strongly influence the speciation, bioavailability and toxicity, and biogeochemical cycling of the metal in the water column. Our benthic flux data show that, in general, the fluxes of Cu, Cd, and Zn and their ligands were higher at station 8 (Norfolk Naval Shipyard) than at station 5 (Norfolk Navy Base), that the relative metal flux order was Zn>Cu>Cd, and that station 8 Cu fluxes were more than 100x greater than in the Chesapeake Bay mainstem. . Furthermore, ligand fluxes exceed metal fluxes, at all sites for almost all metals. Overall, these data will allow us to construct models for the cycling of Cu, Cd, and Zn and their ligands between the sediments and overlying waters and for algal metal uptake and ligand production.

## RELATED PROJECTS

Our work is part of an integrated, collaborative study of the complex processes controlling the concentrations, chemical complexation and speciation, biological uptake, and cycling of three potentially toxic metals (Cu, Cd and Zn) in the Elizabeth River, a major US Naval harbor. As discussed above, our work is carried out in coordination with studies by W. Sunda (NOAA/NMFS) on

the mechanisms and factors controlling algal metal accumulation, and by A. Gordon and J. Donat (ODU) on the *in situ* production of Cu chelators by natural microbial populations in response to elevated Cu levels. Both of these projects are also funded through the ONR Harbor Processes Program.

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